# Processing and optical properties of inorganic–organic hybrids (polycerams). II. PDMS-based waveguides

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## Abstract

Polydimethylsiloxane and the oxides of silicon, titanium and germanium have been incorporated using sol–gel chemistry to yield new polyceram planar waveguides. The waveguides exhibit superior optical properties such as losses as low as < 0.15 dB/cm. The volume homogeneity and optical properties of the films are studied as functions of composition. Sources of attenuation are investigated and related to the volume network and surface characteristics.

## 1. Introduction

Wet chemical techniques offer advantages for the production of homogeneous and high-purity films. This genre of chemistry has recently been used to develop a new class of materials containing both inorganic and organic components. These systems are known as polycerams, ormosils or ceramers, and they exhibit unique properties due to the combination of inorganic and organic functionalities at the molecular level.

Silanol-terminated poly(dimethylsiloxane) (PDMS) is an attractive candidate for the synthesis of polycerams because the terminal $\equiv$ Si–OH groups can condense with oxide precursors to produce metal–O–Si bonds. The mechanical properties of PDMS polycerams have been studied in considerable detail [1–7]. PDMS is known for its superior relaxation properties, and polycerams composed of PDMS experience few cracking problems during drying [1–7]. The structure of PDMS polycerams depends on the pH of reaction, water content and molecular weight of PDMS [1–5]. Small-angle X-ray scattering (SAXS) studies have revealed that high tetraethoxysilane (TEOS) contents and low solution pH result in more homogeneous products [3–5]. In addition, incorporation of titanium alkoxides in the reaction synthesis results in more rapid condensation and further network cross-linking [6,8–10].

These attributes render PDMS-containing polycerams desirable candidates for optical studies. In this study, $SiO_2$–$TiO_2$–PDMS polycerams were studied as passive waveguides. $SiO_2$–Ge-

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$O_2$–PDMS was also examined in parallel to compare the level of homogeneity in both systems. The effect of the inorganic content on the optical properties of both polyceram compositions was investigated and related to the molecular structure. The optical properties studied include the index of refraction, dispersion, UV transmittance and optical attenuation.

## 2. Experimental procedures

Silanol-terminated PDMS polymer (molecular weight (MW) = 400–700) and the alkoxides of silicon together with titanium or germanium were employed to synthesize sol–gel derived polycerams. The precursors used were titanium iso-propoxide ($Ti(O^iC_3H_7)_4$), germanium n-butoxide ($Ge(O^nC_4H_9)_4$) and tetraethoxysilane ($Si(O-C_2H_5)_4$). In the synthesis of solutions, TEOS, PDMS and $H_2O$ (acidified to 0.15M HCl) were first refluxed together. After cool sing, Ti or Ge alkoxides were added and the solution was further refluxed, followed by concentration via rotary evaporation.

A Dektak IIA profilometer was used to measure the film thickness. The index of refraction was obtained using a multi-angle Gaertner ellipsometer equiped with a He–Ne laser. Transmittance spectra were obtained suing a Perkin-Elmer UV–VIS Spectrometer. Dispersion was obtained using a prism-coupling technique to launch laser light into the $TE_0$ and $TM_0$ modes of the waveguide. Measurements were conducted at wavelengths of 632.8, 514.5, 488 and 457.9 nm using helium–neon and argon lasers. Optical loss of the polyceram films was measured using a prism-coupling technique to obtain a streak in the waveguide. These measurements were made using a helium–neon laser ($\lambda = 632.8$ nm), and losses were obtained in dB/cm. The standard deviations in the index of refraction and thickness values lie within ±0.005 and ±0.26, respectively. The details of solution synthesis, processing and characterization of polycerams are contained in an accompanying paper on MPEOU-based waveguides (MPEOU stands for N-triethoxysilylpropyl O-polyethylene oxide urethane) [11].

Table 1
Mole ratios of $SiO_2:TiO_2$ and $SiO_2:GeO_2$ converted to wt % $TiO_2$ and $GeO_2$ in PDMS–$SiO_2$–$TiO_2$ and PDMS–$SiO_2$–$GeO_2$ films

| Molar ratio of $SiO_2:TiO_2$ and $SiO_2:GeO_2$ | wt % $TiO_2$ | wt % $GeO_2$ |
|---|---|---|
| 1:0.5 | 12.9 | 16.2 |
| 1:1 | 19.7 | 25.0 |
| 1:1.5 | 23.7 | 28.9 |
| 1:2 | 26.5 | 32.0 |

All polycerams were composed of 80% by volume polymer (assuming complete hydrolysis/ condensation reactions to yield dense PDMS–$SiO_2$–$TiO_2$ and PDMS–$SiO_2$–$GeO_2$ polycerams). Polycerams were synthesized with $SiO_2:TiO_2$ and $SiO_2:GeO_2$ mole ratios of 1:0.5, 1:1, 1:1.5 and 1:2. Table 1 converts these mole ratios to corresponding weight percentages (assuming the polycerams are composed of dense $TiO_2$ and $GeO_2$ although a small level of residual –OH or –OR groups may still exist in the networks). Since $GeO_2$ (MW = 104.6) has a higher molecular weight than $TiO_2$ (MW = 79.9), the weight percentages of $GeO_2$ in $SiO_2$–$GeO_2$–PDMS are higher than the corresponding weight percentages of $TiO_2$ in $SiO_2$–$TiO_2$–PDMS compositions. The optical properties of polycerams including index of refraction, dispersion and waveguide attenuation were studied as functions of composition and chemistry.

## 3. Results

### 3.1. SiO₂–TiO₂–PDMS

Fig. 1 shows the index of refraction of five compositions of $SiO_2$–$TiO_2$–PDMS. These values were fitted to a linear regression to show that the index of refraction of $SiO_2$–$TiO_2$–PDMS polyceram waveguides increases linearly with increasing $TiO_2$ content. The standard deviations of the index values lie within ±0.005. This dependence of the index of refraction on the $TiO_2$ content suggests that $TiO_2$ is dispersed homogeneously within the PDMS–$SiO_2$ network.
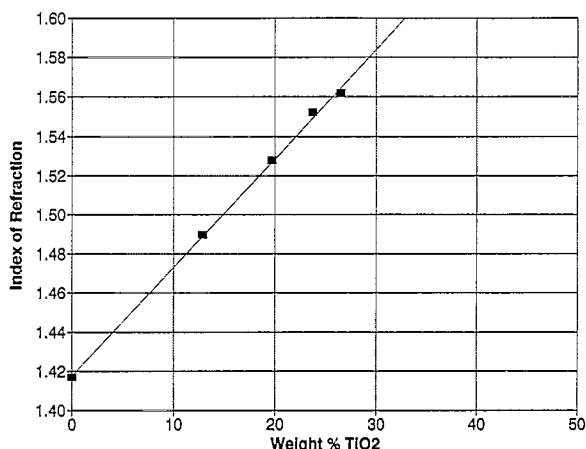
Fig. 1. Index of refraction versus wt % $TiO_2$ in $SiO_2$–$TiO_2$–PDMS polycerams.



Fig. 2. UV transmittance spectra of PDMS–$SiO_2$–$TiO_2$ polycerams.

A planar dielectric waveguide requires that the index of the film be higher than the index of the substrate or the cover. Here, $SiO_2$–PDMS alone has an index of 1.417 which is lower than the index of a quartz substrate, and thus does not exhibit waveguiding. Hence, incorporation of $TiO_2$ in PDMS–$SiO_2$ is necessary to obtain a waveguide.

The highest index of refraction obtained was 1.562 for the polyceram with a $SiO_2$:$TiO_2$ mole ratio of 1:2. Note that $n = 1.562$ is by no means the highest index achievable in PDMS–$SiO_2$–$TiO_2$ polycerams. On the contrary, the weight percentages of PDMS can be lowered to yield waveguides with much higher indices of refraction.

UV–VIS transmission spectroscopy was used to obtain the absorption edge of the polyceram films. As shown in Fig. 2, the wavelength of the absorption edge increases with increasing $TiO_2$ content. The absorption edge of $SiO_2$ (160 nm) is lower than the absorption edge of $TiO_2$ (350 nm). Therefore, as the amount of $TiO_2$ increases, the polyceram incorporates more of the $TiO_2$ characteristics and shows an increase in the absorption edge.

Table 2 summarizes the refractive index and optical attenuation at the He–Ne wavelength ($\lambda = 632.8$ nm) of these waveguides. The thickness of the waveguides was about 1.5 $\mu$m, indicating that crack-free polycerams of high thickness can
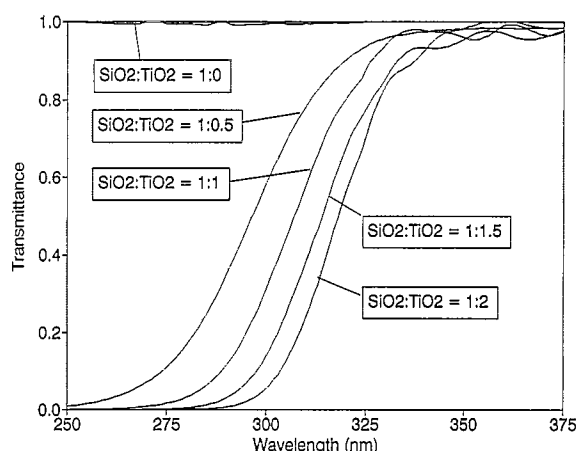
be readily obtained. The optical attenuations of the waveguides range from < 0.15 to 1.23 dB/cm, showing no correlation with composition.

The index of refraction of PDMS–$SiO_2$–$TiO_2$ polycerams versus wavelength was measured using a prism coupling technique where laser light was launched in the $TE_0$ (zero-order transverse electric) and $TM_0$ (zero-order transverse magnetic) modes. Fig. 3 shows the effective index of the $TE_0$ and $TM_0$ modes plotted as functions of wavelength. Measurements could not be conducted on the $SiO_2$–$TiO_2$–PDMS polyceram with a $SiO_2$:$TiO_2$ mole ratio of 1:0.5 because the $TE_0$ and $TM_0$ mode lines were overlapping and they could not be distinguished even with a magnifying lens.

The above values were fitted in the Sellmeier dispersion equation (Eq. (1)) to obtain a linear relationship between the index and wavelength,

Table 2
Refractive index, thickness and loss of PDMS–$SiO_2$–$TiO_2$ polycerams

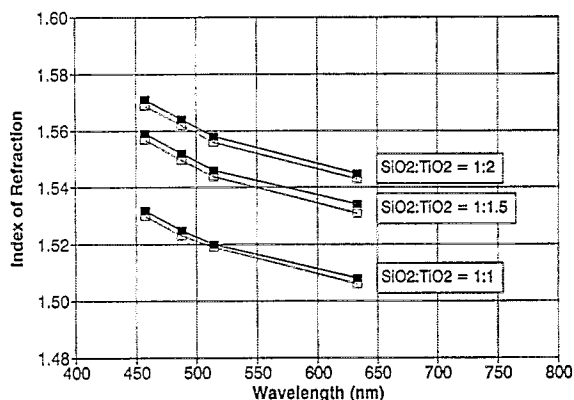| Molar ratio of $SiO_2$:$TiO_2$ in PDMS–$SiO_2$–$TiO_2$ polycerams | Refractive index at $\lambda = 632.8$ nm $\pm$ std. dev. | Thickness $\pm$ std. dev. ($\mu$m) | Loss $\pm$ std. dev. (dB/cm) |
|---|---|---|---|
| 1:0.5 | $1.490 \pm 0.001$ | $1.69 \pm 0.24$ | $1.23 \pm 0.12$ |
| 1:1 | $1.528 \pm 0.001$ | $1.55 \pm 0.18$ | < 0.15 |
| 1:1.5 | $1.552 \pm 0.001$ | $1.42 \pm 0.22$ | $0.87 \pm 0.25$ |
| 1:2 | $1.562 \pm 0.002$ | $1.63 \pm 0.26$ | $0.76 \pm 0.02$ |

Fig. 3. Effective $TE_0$ (■) and $TM_0$ (□) index of refraction of $SiO_2$–$TiO_2$–PDMS polycerams versus wavelength. Lines are drawn as guides for the eye.

Table 3
Dispersion $\Delta n$, and Abbe numbers, $\nu_d$, of $SiO_2$–$TiO_2$–PDMS polycerams

| Molar ratio of $SiO_2$:$TiO_2$ in PDMS–$SiO_2$–$TiO_2$ polycerams | $\Delta n$ $(n_{632.8} - n_{457.9})$ $\pm$ std. dev. | $\nu_d$ |
|---|---|---|
| 1:1 | $0.022 \pm 0.001$ | 31.2 |
| 1:1.5 | $0.024 \pm 0.001$ | 28.21 |
| 1:2 | $0.028 \pm 0.002$ | 24.31 |

and the Abbe number (Eq. (2)) of each composition:

$$\left\{ \left[ n(\lambda)^2 - 1 \right] \right\}^{-1} = A/\lambda^2 + B \tag{1}$$

$$\nu_d = (n_d - 1)/(n_F - n_C). \tag{2}$$

$A$ and $B$ in the above equations are constants which are determined in a least-squares fit, and $n_d$, $n_F$ and $n_C$ are indices for the helium d line (587.6 nm), the hydrogen F line (486.1 nm) and the hydrogen C line (656.3 nm), respectively.

Fig. 4 shows the Sellmeier plots of the polycerams with a goodness of fit, $R^2$ of $> 0.99$, and Table 3 reports the dispersion, $\Delta n$, and Abbe numbers, $\nu_d$, of $SiO_2$–$TiO_2$–PDMS polycerams

obtained as outlined above. A higher dispersion corresponds to a lower Abbe number. The Abbe numbers obtained in this study ($\nu_d = 24.31$–31.52) are in the low range of commercial optical glasses ($\nu_d = 20$–90).

### 3.2. $SiO_2$–$GeO_2$–PDMS

First, an aging study was conducted on a $SiO_2$–$GeO_2$–PDMS polyceram solution with a $SiO_2$:$GeO_2$ mole ratio of 1:1 to study solution stability and homogeneity. Fig. 5 shows the index of refraction (std. dev. of $\pm 0.005$) and thickness (std. dev. of $\pm 0.1$) of this composition as a function of aging. 'Aging' refers to the number of days spent between the synthesis and subsequent spin-coating of solutions. The index of refraction and thickness remained substantially unchanged (fluctuations are within experimental error), indi-
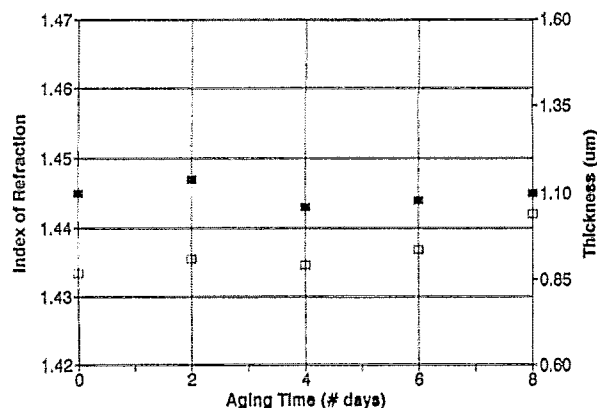


Fig. 4. Sellmeier plots of $SiO_2$–$TiO_2$–PDMS polycerams. ■, $TE_0$; □, $TM_0$.



Fig. 5. Index of refraction (■) and thickness (□) of $SiO_2$–$GeO_2$–PDMS polyceram ($SiO_2$:$GeO_2$ ratio of 1:1) versus aging of solution.
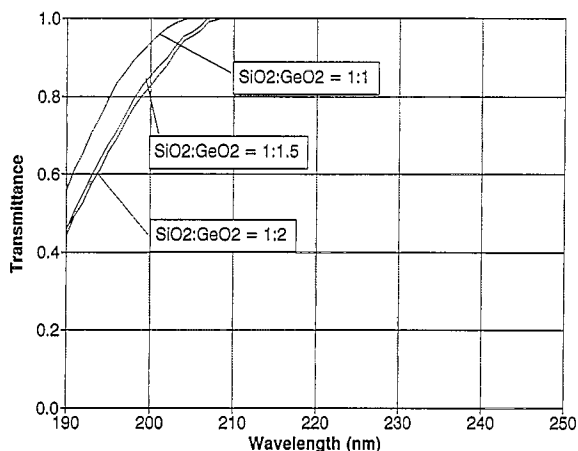
Fig. 6. UV transmittance spectra of $SiO_2$–$GeO_2$–PDMS polycerams.

Table 4
Loss versus TE mode number of a PDMS–$SiO_2$–$TiO_2$ polyceram waveguide with a $SiO_2$ : $TiO_2$ mole ratio of 1:1

| PDMS–$SiO_2$–$TiO_2$ polyceram mole ratio of $SiO_2$ : $TiO_2$ = 1:1 | Loss ± std. dev. (dB/cm) |
|---|---|
| $TE_0$ | < 0.15 |
| $TE_1$ | 3.52 ± 0.207 |

cating that aging of the solution (at least up to 8 days) did not affect the network homogeneity.

UV–VIS spectroscopy was employed to determine the wavelengths of the absorption edges of $SiO_2$–$GeO_2$–PDMS films. As shown in Fig. 6, the absorption edges fall outside the measured regime, indicating that all $SiO_2$–$GeO_2$–PDMS compositions exhibit 100% transmittance at least to a wavelength of ~ 210 nm. The absorption shoulder of $SiO_2$–$GeO_2$–PDMS with a $SiO_2$ : $GeO_2$ mole ratio of 1:0.5 was lower than the measured range, indicating that since the polyceram contained more $SiO_2$, it exhibited more of the $SiO_2$ behavior ($SiO_2$ absorbs at 160 nm).
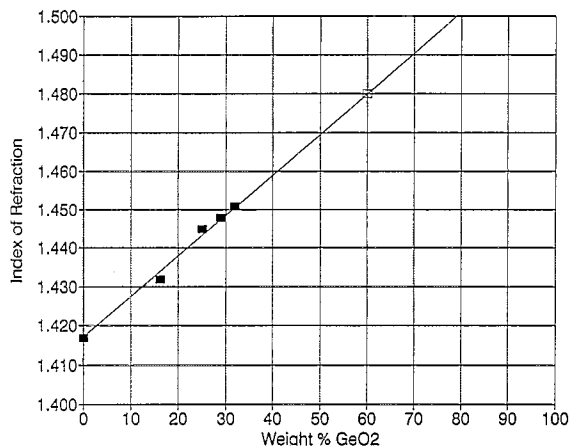
The index of refraction of $SiO_2$–$GeO_2$–PDMS compositions was then studied as a function of inorganic content. Fig. 7 shows the index of refraction of five compositions of $SiO_2$–$GeO_2$–PDMS polycerams with a standard deviation of ± 0.005. A linear fit through these values indicates that the index of refraction increases with increasing $GeO_2$ content. However, the increase is relatively small and a $SiO_2$–$GeO_2$–PDMS polyceram of 32 wt% $GeO_2$ content has an index of refraction of only 1.451. Calculations revealed that for a $SiO_2$–$GeO_2$–PDMS waveguide of 1.4 μm thickness to support only the zero-order modes on a substrate of $n = 1.46$, a film index of 1.48 is required. As shown in Fig. 7, this index corresponds to 60 wt% $GeO_2$. Although the synthesis of a polyceram composition of 60 wt% $GeO_2$ content was successful, the surface of the film was not smooth after spin-coating. This increased surface roughness indicated that the large quantity of inorganic content retarded the relaxation abilities of the network.

## 4. Discussion

The optical properties of waveguides are manifestations of their molecular networks. The optical losses of $SiO_2$–$TiO_2$–PDMS waveguides are surprisingly low considering the number and disparate nature of the constituents. These low losses are indicative of high volume homogeneity and low surface roughness. A loss of < 0.15 dB/cm is comparable with that of the best planar waveguides ever synthesized [12,13].

In order to determine the source of scattering in the $SiO_2$–$TiO_2$–PDMS waveguides, a study of loss versus mode number was conducted. The sample chosen had a $SiO_2$ : $TiO_2$ ratio of 1:1,
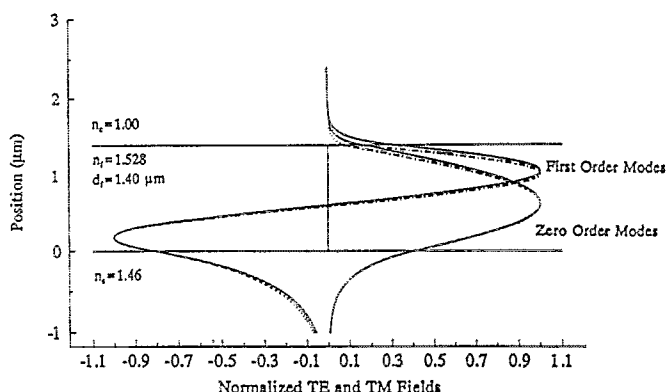


Fig. 7. Index of refraction versus wt% $GeO_2$ in $SiO_2$–$GeO_2$–PDMS polycerams.

Fig. 8. Transverse electric and magnetic profiles of a $SiO_2$–$TiO_2$–PDMS polyceram with a $SiO_2$–$TiO_2$ mole ratio of 1:1. ·–·–·, TM; ———, TE.

and losses were measured on the $TE_0$ and $TE_1$ mode lines. Table 4 shows that the loss increased noticeably from $< 0.15$ dB/cm at $TE_0$ to 3.52 dB/cm at $TE_1$.

To correlate this 'higher mode–higher loss' relationship to surface or volume scattering, the transverse electric (TE) and magnetic (TM) field profiles of the above $SiO_2$–$TiO_2$–PDMS composition were calculated. Fig. 8 shows the TE and TM field profiles of the polyceram waveguide with an index of 1.528 and a thickness of 1.4 μm. As the mode number increases, the portion of the electric and magnetic field profiles propagating outside the guiding region also increases. The $TE_1$ and $TM_1$ modes probe the surface of the film to a higher extent than the $TE_0$ and $TM_0$ modes. Lower-order modes have most of their energy confined within the guiding layer. Hence, the increase of loss with increasing mode number implies that most of the losses in the $SiO_2$–$TiO_2$–PDMS system originate from surface scattering.

$SiO_2$–$TiO_2$–PDMS waveguides stand by contrast with $SiO_2$–$TiO_2$–MPEOU waveguides where losses are believed to be caused by volume inhomogeneities [14]. Although volume scatterings can be reduced through increased cleanliness and careful processing, surface scattering can be reduced more easily by incorporating chelating agents. An earlier study on the surface morphology of MPEOU-based waveguides showed that the surface roughness can be decreased notice-

ably (14 Å to 4 Å root mean square roughness) by the incorporation of 2,4-pentanedione as a chelating agent [15]. The same chelating procedure can thus be applied to PDMS-based waveguides to increase the smoothness of the surface and reduce surface scattering.

Losses of $SiO_2$–$TiO_2$–PDMS waveguides were also measured as functions of wavelength. The sample chosen had a $SiO_2$:$TiO_2$ mole ratio of 1:1. Fig. 9 shows losses measured at $\lambda = 632.8$, 514.5, 488 and 457.9 nm. A power fit through these values shows a $\lambda^{-15}$ loss dependence with a goodness of fit, $R^2$, of 0.85. The $\lambda^{-15}$ loss dependence is far from the $\lambda^{-4}$ relation expected for Rayleigh scattering. UV–VIS transmission spectroscopy did not indicate any absorption peaks in
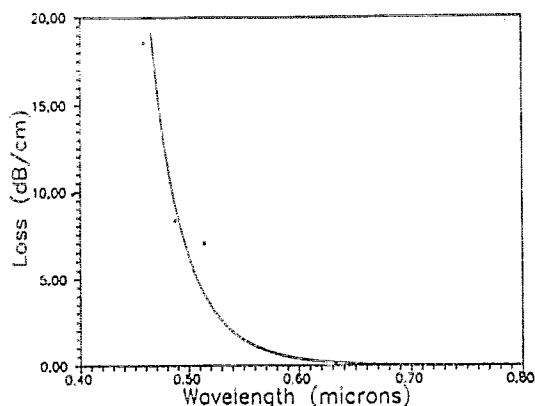


Fig. 9. Loss versus wavelength of a $SiO_2$–$TiO_2$–PDMS polyceram with a $SiO_2$:$TiO_2$ mole ratio of 1:1.

the yellow–orange region ($\lambda = 580–600$ nm), which would indicate the existence of $Ti^{3+}$. However, a bulk piece of $SiO_2$–$TiO_2$–PDMS turned dark blue ($\lambda = 450–500$ nm) after long exposure to the ambient atmosphere, implying possible reduction of $Ti^{4+}$ to $Ti^{3+}$. This reduction mechanism may be the cause of the sudden increase in attenuation at shorter wavelengths.

## 5. Conclusions

$SiO_2$–$TiO_2$–PDMS and $SiO_2$–$GeO_2$–PDMS polycerams were successfully synthesized using sol–gel techniques. Both compositions revealed a steady increase of the index of refraction and the absorption edge with increasing inorganic content. Although $SiO_2$–$GeO_2$–PDMS polycerams never achieved the required index to exhibit waveguiding capabilities, $SiO_2$–$TiO_2$–PDMS polycerams showed outstanding waveguiding properties. The chemistry and processing of the latter were optimized to yield $SiO_2$–$TiO_2$–PDMS polycerams with losses as low as $< 0.15$ dB/cm. Scattering studies indicated that surface roughness makes a strong contribution to the optical loss of $SiO_2$–$TiO_2$–PDMS waveguides. This implies that losses can be reduced even further by controlling the surface morphology through chemistry (i.e., incorporation of chelating agents).

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